

CIDNP STUDY OF REACTIONS OF KETYL AND DIANIONS DERIVED FROM BENZOPHENONE AND FLUORENONE WITH ACETIC ANHYDRIDE

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Abstract—A study is presented of ^1H and ^{13}C CIDNP effects in the reactions of Na and Li salts of ketyls and dianions derived from benzophenone and fluorenone with acetic anhydride in tetrahydrofuran and dimethoxyethane. CIDNP effects were observed for products obtained by mixing of reactants both at high and at low field. Interpretation of the CIDNP effects (mixing at high field) indicates that in reactions of ketyls with acetic anhydride the primary step is *O*-acylation followed by spin-selective electron transfer between ketyl and *O*-acylated ketyl. At higher dilution or in the presence of strongly coordinating agents, heterolytic deprotonation of acetic anhydride by ketyl is also observed. CIDNP effects depend on the presence of ketyl which affects the relaxation of sterically accessible nuclei and also suppresses the intensity of ketone signals by rapid electron transfer. In reactions of dianions, electron transfer between dianion and acetic anhydride partly takes place, and the ketyl formed in this way reacts with a further molecule of acetic anhydride.

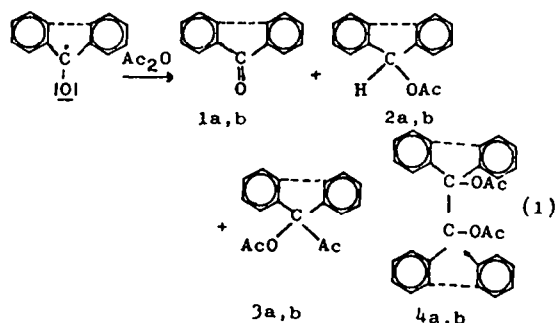
Our knowledge of the reactions of ketyls with molecules with a closed electron shell is rather incomplete, in spite of the fact that this class of reactions is important both for organic and for macromolecular chemistry.¹⁻⁷ The best studied are the reactions with alkyl halogenides,¹⁻³ where the electron transfer mechanism has been proved.³ Attention has also been paid to esters, aldehydes and nitriles, especially in connection with studies of ketyl-initiated polymerizations of monomers carrying these functional groups.⁴⁻⁶ For these reactions, the proposed mechanism was mostly electron-transfer,^{4,5} or heterolytic deprotonation of substrate by ketyl or dianion produced by a dismutation reaction.⁶

In summing up it can be stated that most published studies of ketyl reactions are concerned with "soft" acceptors, where the electron-transfer mechanism may be expected with some probability. On the other hand, in the case of "hard" acceptors, a mechanism with nucleophilic addition or substitution seems to be more acceptable. For deciding this problem, few data are available in the literature so far. A mechanism assuming the $\text{S}_{\text{N}}2$ reaction as a primary step was proposed for "trapping" of electrochemically generated ketyls by acetic anhydride⁸ or by chlorides of carboxylic acids.^{9,10}

A preliminary study of the reaction of chemically generated ketyl (lithium salt of benzophenone ketyl) with acetic anhydride (Ac_2O) was presented in a previous paper of one of us⁷ in connection with a study of reactions of dianions derived from diarylketones. The finding that this reaction leads to a relatively simple mixture of products (compounds **1a**, **2a** and **3a** in eqn (1) correspond to 93% of yield), and that the ^1H NMR spectrum measured immediately after mixing the reactants in a low magnetic field exhibits emission signals of compound **2a** corresponding evidently to CIDNP, indicated that the mechanism could be clarified by a more detailed study.

Besides contributing to our knowledge of the mechanism of ketyl reactions, such a study seemed justified even for the sake of the CIDNP method itself which has so far been systematically applied in the field of stable anion-radicals only by Garst *et al.*¹¹ who studied the reactions of naphthalene sodium. In these studies, only ^1H NMR spectroscopy was used, with mixing of reactants in low magnetic field. We assumed that a study of the reactions of structurally quite different types of anion radicals and the application of both ^1H and ^{13}C NMR spectroscopy could contribute to an expansion of possibilities and definition of applicability of the CIDNP method in studies of reactions of stable ion-radicals.

Therefore we considered as useful a systematic study of CIDNP effects in reactions of ketyls (and of dianions for comparison) of two typical representatives, benzophenone and fluorenone with Ac_2O :



a benzophenone, b fluorenone (bond shown by dotted line)

In the reactions we varied the conditions of the reaction itself (metal used in preparation of the reactant, reaction medium, ratio of reactant and substrate concentrations) and the mode of measurement (application of ^1H and ^{13}C NMR spectroscopy). For studies of the effects in ^{13}C NMR spectra, a continuous-flow NMR cell was constructed.

ted, making possible mixing and homogenization of reaction components and flow measurement of the reacting mixture.¹²

EXPERIMENTAL

Chemicals and solvents. Commercial Ac_2O was purified by reactivation. Tetrahydrofuran (THF) was purified by means of LiAlH_4 and dimethoxyethane (DME) by means of the sodium salt of benzophenone dianion. Distillation of solvents and preparation of solutions of ketyls and dianions and all manipulations with these solutions were performed in argon atmosphere. Solutions of dianions were prepared by reactions of ketones with a fivefold (molar) excess of metal (Li, Na), the solutions of ketyls by a reaction of an equimolar amount of metal and ketone. Concentration of ketone in solvent (THF, DME) in these preparations was 0.1 or 0.2 M, in measurements of CIDNP effects the concentration of ketyls was modified according to need by a subsequent dilution of the solution. Strongly co-ordinating agents used: 15-crown-5 (Fluka) dried by sodium hydride and distilled at reduced pressure; Cryptands C211, C221 and C222 (Merck trade name Kryptofix 211, 221 and 222).

Compound **2a** was prepared by acetylation of diphenylmethanol by acetic anhydride, the preparation of compounds **3a** and **2a-4b** is described in Ref. 7. Further compounds which could be formed in the studied systems, were prepared as follows.

1-Hydroxy-1,1-diphenylpropan-2-one. To a soln of 2.55 ml of methyl acetate in 20 ml THF, 67 ml of 0.263 M solution of dilithium benzophenone in THF was added dropwise with stirring, and the mixture was further stirred for 2 h. After evaporation of THF the residue was treated with water and extracted into ether. The residue from the ether phase was chromatographed on silica gel (petrol ether-ether 9:1) and the residue of the main fraction was distilled at reduced pressure (1.76 g, 52%); the purity of the product was verified by elemental analysis and by NMR spectroscopy.

1,1-Diphenylpropane-2-one: the compound was prepared from diphenylacetylchloride¹³ by malonate synthesis.¹⁴

¹H CIDNP spectra were measured by means of the spectrometer PS-100 (JEOL). The reactants were mixed at low field by the procedure described by Garst,¹⁵ but instead of mixing in a Helmholtz coil, the samples were mixed near to the NMR magnet. For mixing at high field ($H_0 = 24$ kG), a cell with a T-cock was placed in the spectrometer probe head, and by means of polythene capillaries and syringes in a stream of argon, 0.3 ml of 0.1 M solutions of both reaction components were injected simultaneously.

¹³C CIDNP NMR spectra were measured by means of the spectrometer FX-60 (JEOL) in a continuous-flow cell, making possible simultaneous introduction of the solutions of both reaction components and mixing of the reacting mixture. In this case vigorous stirring of the mixture is necessary because an insoluble salt of acetic acid is formed during the reaction; this creates an impermeable boundary between the two solutions which prevents diffusion of both reacting components. The solutions were introduced into the cell by means of two glass syringes placed in a linear doser with an adjustable velocity of flow. The system made possible accumulation of spectra and performance of the reactions in inert atmosphere (Ar). The solutions were mixed directly in the spectrometer probe ($H_0 = 14.5$ kG), a detailed description of the continuous-flow cell and its application will be given in a separate communication.¹²

All measurements of ¹³C CIDNP spectra were repeated several times (3-7 ×) in order to verify the reproducibility of the results. In the basic type of experiment, the concentration of the generated compounds was so low that their NMR spectrum could not be obtained even at much longer accumulations than those used in CIDNP measurements.

The composition of the reaction mixture after the CIDNP experiment was determined in the following way. After evaporation of the solvent (THF, DME) the residue was

treated with water (in experiments with cryptands, dilute hydrochloric acid was used instead of water) and extracted with ether. The extract was evaporated and vacuum dried (oil pump) for 30 min. The mixtures of products obtained in this way were quantitatively analyzed by ¹H NMR, in the form of 10% (v/v) solutions in CDCl_3 using the Varian XL-200 spectrometer.

RESULTS

¹H CIDNP NMR Spectra

CIDNP effects observed during the mixing of reactants in high field (HF) and in low field (LF) in the reaction of benzophenone ketyl (BFNa, in THF) are shown in Fig. 1. With mixing in HF, (Fig. 1a) an effect was observed only in the range of aromatic protons. An enhanced absorption peak is observed in the range of the signals of compounds **1a-3a**, whereas an emission peak is observed in the range of the signals of compounds **2a** and **3a**. With mixing of reactants in LF (Fig. 1b), only emission signals are observed in a range which is common for aromatic protons of compounds **2a** and **3a**, and in the range corresponding to the proton on C-1 of compound **2a** (for the numbering of various carbons see Fig. 2). The changes caused by change of metal (Li) are comparable with the variability of individual measurements. Analogous but smaller effects were observed also in reactions of the dianions (BFLi and BFNa in THF).

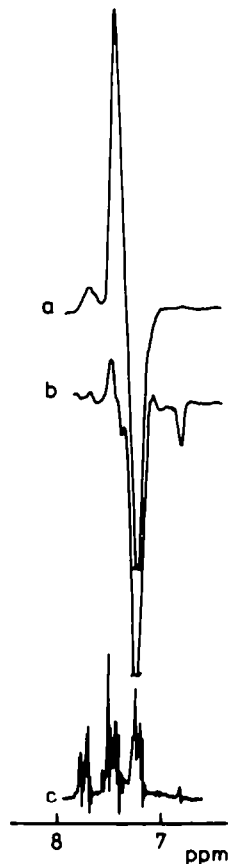


Fig. 1. ¹H CIDNP spectra of the mixture of benzophenone sodium ketyl and acetic anhydride (molar ratio 1:1) in tetrahydrofuran measured (a) after mixing in the probe of spectrometer, (b) after mixing in low field, and (c) measured after completion of reaction.

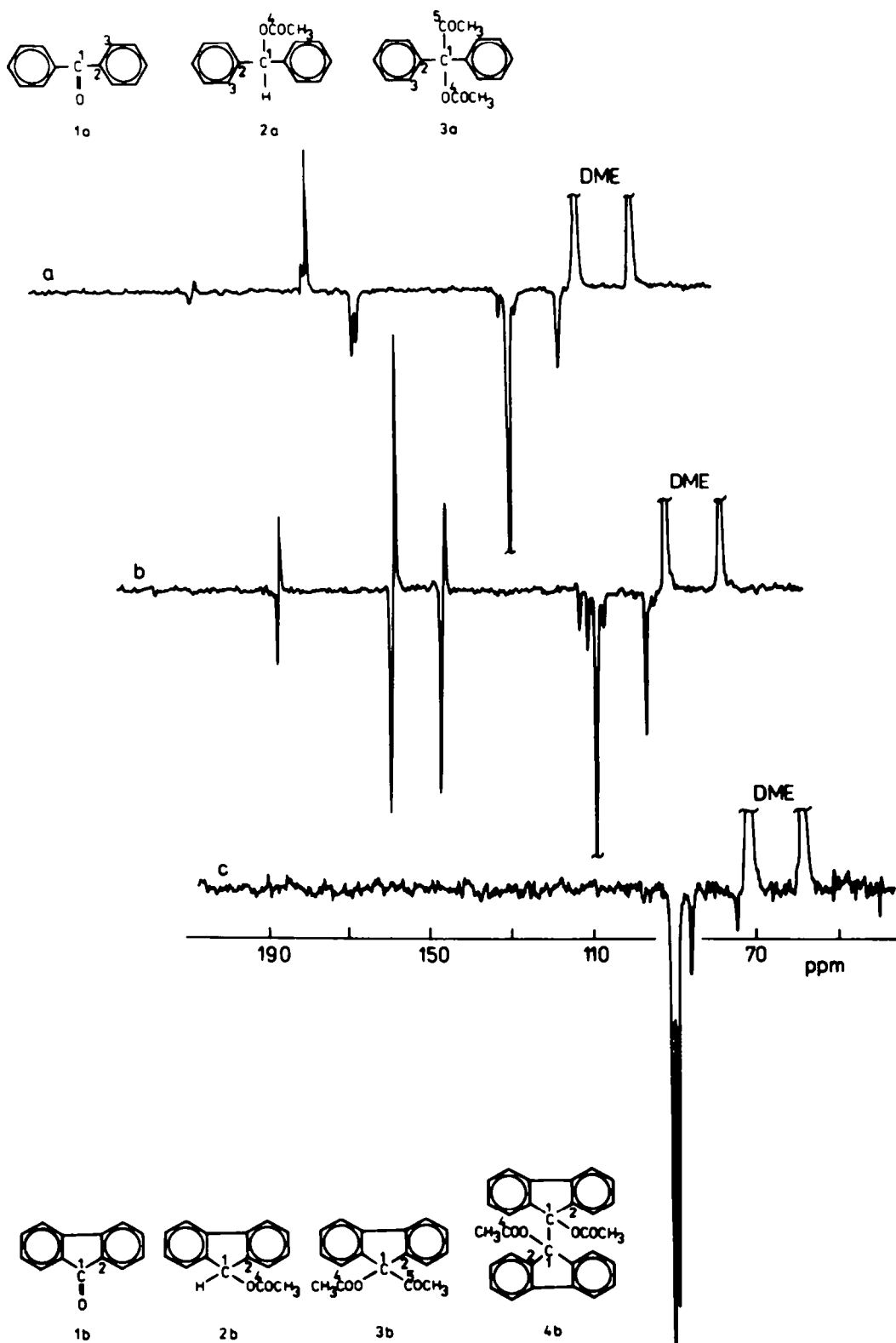


Fig. 2. ^{13}C CIDNP spectra measured during the reactions of ketyls with acetic anhydride (molar ratio 1:1) in dimethoxyethane, total concentration of reactants in the mixture 0.05 M, (a) benzophenone lithium ketyl, (b) benzophenone sodium ketyl, (c) fluorenone sodium ketyl.

In studies of CIDNP effects in reactions of the derivatives of fluorenone, a weak effect was observed only in the reaction of the sodium salt of fluorenone ketyl (FLNa in THF) with mixing in LF in the range of aromatic protons. In the analogous reaction, when the solutions were mixed in HF, similarly as in reactions of dianions (both LF and HF in THF) no CIDNP effect was observed.

¹³C CIDNP NMR Spectra

As can be seen from the above mentioned results obtained by measurement of ¹H CIDNP spectra, all signals cannot be definitely assigned to the corresponding compounds generated in the studied reactions. Therefore these reactions were also studied by ¹³C NMR spectroscopy, where all signals could be clearly assigned thanks to the larger differences in chemical shifts of the compounds concerned. This assignment was achieved by a comparison of the spectrum of the mixture with the spectra of the pure compounds **1a–3a** and **1b–4b**. The chemical shifts of the carbons of these compounds which exhibited a CIDNP effect, are summarized in Table 1 (compound **4a** cannot be prepared because of its instability; its formation in the reaction was suggested by the appearance of an additional emission signal in the range of C-1, which was assigned to structure **4a** by analogy with compound **4b**).

Signals corresponding to further compounds which could be generated in the reactions (i.e. diphenylmethanol, 1,1-diphenylpropane-2-one and 1-hydroxy-1,1-diphenylpropane-2-one) were not found in the CIDNP spectra.

The results obtained by measurement of ¹³C CIDNP effects in the basic experiments are qualitatively summarized in Table 2; some of the spectra are reproduced in Figs. 2. In these cases, the CIDNP spectra can be affected by many factors. Before detailed interpretation, we wish to point out the most

Table 1. ¹³C NMR chemical shifts (ppm from TMS) of carbons exhibiting CIDNP effect in compounds **1a–3a** and **2b–4b**

Compound	Carbon				
	1	2	3	4	5
1a	195.3	138.2	130.1		
2a	76.8	141.3	127.3	169.2	
3a	89.3	140.0	128.6	169.5	200.9
2b	75.1				
3b	91.3				
4b	90.1	141.6			

important relations which follow from a comparison of the results.

(i) CIDNP effects observed in reactions of benzophenone and fluorenone derivatives (ketyls and dianions) on C-1 of compounds **2a** and **3a** and **2a–4b** are in all cases emission signals, for compound **1a** the effect, if any, on C-1 is always enhanced absorption.

(ii) In reactions of benzophenone ketyls and dianions with Ac₂O for compounds **2a** and **3a**, besides the effects on C-1, effects can also be observed on C-4 (the effect depends on reaction conditions) and weak effects on C-5 of compound **3a** (always emission).

(iii) Changes in reaction conditions (change of metal, change of reaction medium, change of concentration of reactants) mostly affect CIDNP effects on compound **2a**.

(iv) Lowering of the concentration of reactants (down to 0.005 M) in reactions of benzophenone ketyls suppresses effects on compound **3a**, its concentration in the mixture also decreases, while the ratio

Table 2. CIDNP effects on various carbons of compounds **1a–3a** and **1b–4b** in reactions of sodium and lithium ketyls (BFNa, BFLi and FLLi) and of dianions (BF₂Na, BF₂Li and FL₂Na) with acetic anhydride in dimethoxyethane (DME) and tetrahydrofuran (THF). Molar concentration of reactants and acetic anhydride in the ratio 1:1 with ketyls and 1:2 with dianions. Total concentration of reactants in the mixture 0.05 M. A—enhanced absorption, E—emission

Reaction	Compound / Carbon															
	1a,b			2a,b					3a,b				4a,b			
	1	2	3	1	2	3	4	1	2	3	4	5	1	2	3	4
BFLi, DME	-	-	-	E	A	E	-	E	A	E	E	E				
BFLi, THF	-	-	-	E	A	E	-	E	A	E	E	E				
BFNa, THF	A	E	A	E	A	E	E	E	A	E	E	-				
BFNa, DME	-	-	-	E	E	A	A	E	A	E	E	E				
BF ₂ Li, THF	-	-	-	E	A	E	-	E	A	E	E	-				
BF ₂ Na, THF	A	E	-	E	E	A	A	E	A	E	E	-				
BF ₂ Na, DME	-	-	-	E	E	A	A	E	A	E	E	E				
FLNa, FLLi, DME	-	-	-	E	-	-	-	E	-	-	-	-				E
FLNa, FLLi, THF	-	-	-	E	-	-	-	E	-	-	-	-				E
FL ₂ Na, DME	-	-	-	E	-	-	-	E	-	-	-	-				E

of concentrations $2a + 3a:1a$ remains constant at 1:1. Suppression of effects on the carbons of $3a$ also takes place by the action of strongly coordinating agents (crowns, cryptands); in this case compound $3a$ is not found in the mixture after reaction.

(v) An increase of the concentration of Ac_2O at constant concentration of benzophenone ketyl leads to a suppression of effects on compound $2a$ and an increase of effects on compound $1a$. The ratio of compounds in the reacted mixture, $2a + 3a:1a$ is always equal to 1:1.

(vi) In cases where in the normal experimental procedure effects were observed on $1a$ (BFNa and BF₂Na in THF), an excess of benzophenone (added to the solution of ketyl or to the solution of Ac_2O in reaction with dianion) leads to an increase of CIDNP effects on C-1 and -2 of compound $1a$. Besides that, at a large excess of benzophenone, a normal spectrum of the other benzophenone carbons can also be observed, and the intensity of the corresponding peaks is almost equal with the spectrum of the reacted mixture measured by the flow method under the same conditions.

On the other hand, in cases where CIDNP effects on $1a$ have not been observed (BFLi and BF₂Li in THF), in the spectrum measured during the reaction, signals of benzophenone have not been observed even at 12 fold excess.

(vii) 12 fold molar excess of fluorenone in the solution of sodium fluorenone ketyl (DME) promotes the CIDNP effect on C-1 of compound $4b$ and almost suppresses effect on carbon 1 of compound $3b$. Besides that, a CIDNP effect on C-2 of compound $4b$ can be observed (enhanced absorption). Signals of fluorenone were not observed in the spectrum, even when its concentration was sufficient.

DISCUSSION

Three possible mechanisms of the reaction of ketyls with electrophilic agents have been already discussed in the literature,³⁻⁷ considering as primary reaction (a) an attack of the agent on the nucleophilic centre of the ketyl (eqn 2a); (b) a dismutation reaction between two molecules of ketyl with the generation of a highly reactive dianion (eqn 2c); or (c) a mono-electron transfer from the ketyl to the agent.

In considerations of reactivity, solvation has to be considered. By means of ESR and optical measurements it was found that ketyls in THF or DME exist in predominantly monomeric form only at concentrations 10^{-4} M or lower; at higher concentrations they are associated to paramagnetic dimers or higher associates.¹⁶ An analogous study of the effect of cryptands on solutions of alkali salts of fluorenone ketyls lead to the conclusion that in this case the ketyl is present in monomeric form, as a contact pair of the ketyl anion and of the cryptand complex of the cation.¹⁷ In the case of the combination of the sodium salt of the fluorenone ketyl and C222 in DME medium, an equilibrium between contact pairs and "cryptand separated ion pairs" has been observed.¹⁷

The effect of solvation conditions on reactions of ketyls with acylating agents has not been studied so far.

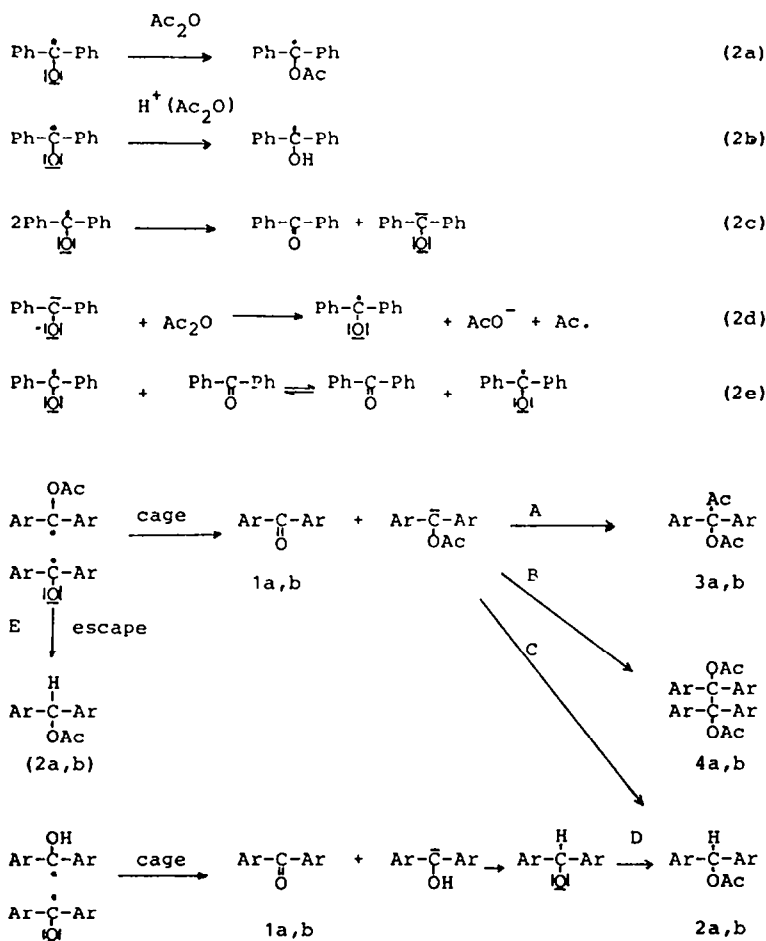
In the presence of strongly co-ordinating agents of

the type of crowns and especially cryptands, dissociation of ketyl to monomer and separation of the counterion by ligand leads to a pronounced stripping and partial localization of the electron density on oxygen which in the primary step makes possible heterolytic deprotonation of Ac_2O by ketyl, and which can also promote the otherwise improbable electron transfer (mechanism c, large difference of polarographic half wave potentials¹⁰).

In view of the above mentioned ideas about the reaction mechanisms of ketyls and data about solvation conditions we have attempted to interpret the results of CIDNP measurements.

A typical ¹³C CIDNP spectrum measured during mixing of solutions of BFLi and Ac_2O in DME is shown in Fig. 2(a). Similar spectra were also measured for the systems BFLi and BFNa in THF and BF₂Li in THF. In all the cited reactions CIDNP spectra exhibited the same polarization phase on the carbons with the same numbering in compounds $2a$ and $3a$, and a reversed phase on the corresponding carbons of compound $1a$ (in reactions of BFLi in THF and DME the effects on compound $1a$ were observed only at excess of Ac_2O). All compounds ($1a-3a$) exhibit opposite phase of polarization on neighbouring carbons. The same effect was also observed in the photochemical reaction of benzophenone in the presence of a proton donor.¹⁸ As already mentioned, under these reaction conditions, nucleophilic substitution leading to an acylated radical is the most probable (eqn 2a). At the studied concentrations, the ketyls are present as paramagnetic associates.¹⁶ Therefore the encounter of an acylated ketyl with an untreated ketyl is highly probable. In the radical pair generated in this way, spin selective electron transfer can take place (the acylated ketyl is a better acceptor) under formation of polarized benzophenone and polarized diamagnetic anion, yielding by further reaction the products $2a$, $3a$ and probably also $4a$ (see reaction Scheme 1, path A, C and B). An analogous mechanism of formation of compound $3a$ is also assumed in polarography of benzophenone in the presence of Ac_2O in acetonitrile medium,⁸ provided that under these conditions the acylated radical is not reduced by free ketyl, but by further electroreduction.

The phase of the polarization generated by the spin-selective process is a function of the parameters describing the radical pair and the process of formation of the diamagnetic product from the radical pair. For the net effect, Kaptein formulated a relation between the sign of the polarization and these parameters in the form of binary formula $\Gamma_{net} = \epsilon\mu A_1 \Delta g$,¹⁹ in which μ designates the multiplicity of the radical precursor, ϵ the way of product formation from the radical pair, A_1 the hyperfine coupling constant between the considered nucleus and the electron, and Δg the difference of g-factors of the radicals forming the pair. Our type of radical pair, ketyl-acylated ketyl, is formed by the encounter of free radicals ($\mu = +$), the acylated anion is formed by electron transfer as a cage product ($\epsilon = +$), the hyperfine coupling constant between carbon 1 and electron is positive ($A_1 = +$).²⁰ The g-factor of the ketyl radical (alkali salt) is 2.0037²¹ and the g-factor of the acylated radical may be expected, in analogy with the diphenylhydroxymethyl radical ($g = 2.0030$),²² to be



Scheme 1.

smaller than for the ketyl radical ($\Delta g = -$). For the polarization on carbon 1 of the generated acylated anion we then obtain $\Gamma_{\text{net}} = + + + - = -$, i.e. an emission CIDNP signal. The reactive acylated anion then reacts further with acetic anhydride under formation of compound **3a** (reaction Scheme 1, path A), or by path C (deprotonation of Ac_2O) under formation of compound **2a**, or possibly by reaction with benzophenone and subsequent acylation (path B) to compound **4a** (with benzophenone ketyls this reaction is rare).

Similarly as with the pair ketyl-acylated ketyl, the spin-selective electron transfer can also take place in the pair ketyl-protonated ketyl. The diphenylhydroxymethyl radical (protonated ketyl) is a better acceptor than the alkali salt of ketyl. The formation of protonated ketyl according to eqn (2b) is important mainly in the presence of coordinating agents (crowns, cryptands), or at larger dilution of the solution, but it cannot be excluded even in reactions proceeding under normal conditions. Compound **2a**, generated from the radical pair ketyl-protonated ketyl by path D (Scheme 1) must exhibit the same phase of polarization as the compounds **2a** and **3a** formed by path A or C, because the parameters of the Kaptin formula for net-effect are equal for both these cases.

Compounds **2a** and **3a** must exhibit the same phase

of polarization on equally numbered carbons, whereas in compound **1a** polarization of the corresponding carbons is reversed. This is in agreement with the experimental results obtained for the systems BFLi in DME and THF, BFNa in THF and BF2Li in THF in reaction with an equimolar amount of Ac_2O .

The effects on compound **1a**, especially on C-1, are strongly affected by electron transfer between benzophenone and ketyl (eqn 2e), which is especially important in the case where acylation (eqn 2a) is slow and the mixture contains a relatively high concentration of unreacted ketyl (see point 7). This is in agreement with the observation that the effects on benzophenone appear or increase when excess of acetic anhydride is used (see point 6). The lowering of the effects on benzophenone can be also partly prevented by addition of a larger amount of benzophenone to the original ketyl (see point 7).

In the reaction of BFNa with Ac_2O in DME the phase of polarization on carbons 1 is the same as with the systems previously discussed, but compound **2a** exhibits a reversed phase of polarization on the remaining C-2-4 (see Fig. 2b and Table 2). We assume that compound **2a** is formed partly by path C and D (Scheme 1) and besides that also as an escape product by reaction of the radical with the solvent by path E (Scheme 1). Compound **2a** formed

by path E must have opposite polarizations to those formed by path C or D. The competition of these mechanisms together with different relaxation mechanisms of nuclei in the escape-radical and in the cage-anion is the reason why **2a** exhibits emission on carbon 1, but the phase of polarization on the remaining carbon is opposite to that expected from the alternating signs of hsc (see Ref. 18). (Relaxation of nuclei in the diamagnetic acylated anion is probably considerably affected by the presence of unreacted ketyl which acts more strongly on the accessible nuclei 2, 3, 4 and 5 than on the sterically hindered C-1). CIDNP effects in this reaction are strongly affected by addition of cryptand (C222 or C221) to the solution of ketyl (BFNa in DME). The effects on the carbons of **3a** are in this case almost suppressed, and the effects on carbons of **2a** increase strongly, while the polarization on carbons 2, 3 and 4 is reversed as compared to that in the absence of cryptand. Besides the signals of compound **2a**, strong effects were also observed on signals corresponding by their chemical shift to compound **1a**, particularly C-2 (emission) and C-3 (enhanced absorption). (The fact that no effect was observed on C-1 of compound **1a** is probably again connected with the reaction **2e** which affects mostly just this carbon). The phase of polarization on all observed carbons of compounds **1a** and **2a** is consistent with the idea about the formation of these compounds by path D from the protonated ketyl. The negligible yield of compound **3a** and weak CIDNP effects on its carbons can be explained by the predominance of mechanism D.

From CIDNP spectra, a similar reaction course can be also expected for the reactions of dianions. However, in this case the above mentioned mechanisms are preceded by electron transfer from dianion to acetic anhydride (eqn 2d) which was proved by measurement of ESR spectra of solutions of dianions after addition of solution of Ac_2O (molar ratio 1:1.3) and where strong ketyl signals were found.⁷ Besides that it is highly probable that reactions proceeding by polar mechanism, like C and O acylation and acidobasic reaction, also participate in the overall course.⁷ These reactions are not manifested in NMR spectra by CIDNP effects, but they can affect them indirectly. Differences in CIDNP effects of dianions and ketyls (for some metal in the reactant and same solvent) which are considerable between BFNa and BF₂Na in THF, are probably caused by a different ratio of the rate of electron transfer from dianion to Ac_2O and acylation of the formed ketyl. This ratio determines at which ketyl concentration reactions responsible for CIDNP effects take place.

In reactions of fluorenone ketyls and dianions, effects were only observed on C-1 of compounds **2b**, **3b** and **4b** (see point 1), and besides that emission signals also appeared at positions which did not correspond to any compounds expected to occur in the reaction mixture. We assume that these signals correspond to a dimer product, acylated only on one oxygen. The reactions of fluorenone ketyls with Ac_2O are slower than the analogous reactions of benzophenone ketyls. Reactions leading to CIDNP effects are expected to be similar as with benzophenone derivatives. As the rate determining step of the reaction is acylation (or protonation) of ketyl, reac-

tions leading to CIDNP effects will in this case proceed at higher concentration of unreacted ketyl as compared to the benzophenone derivatives. The occurrence of CIDNP effects only on C-1, i.e. on sterically hindered carbons, and the absence of effects on the other carbons is in agreement with the proposed effect of unreacted ketyl on the relaxation of nuclei in the polarized diamagnetic anion generated by electron transfer.

An analysis of the phase of polarization by means of the Kaptein relation for the net effect (the parameters are identical with those for the benzophenone derivatives)²⁴ indicates that the CIDNP effects on the products **2b**, **3b** and **4b** originate in the reaction by path C (possibly D), A and B. The dimer product **4b** could be also generated by direct combination of the radical pair ketyl-acylated ketyl and subsequent acylation, but in this case the CIDNP effect would probably be cancelled out. The proof that the main mechanism of formation of **4b** is the path B (Scheme 1) are the results of CIDNP measurements during the reaction of FLNa with Ac_2O in DME, where a twelvefold excess of fluorenone has been added to the solution of ketyl (see point 8). The effect on compound **3b** is in this reaction almost suppressed and effects are only observed on compound **4b** (emission on carbon 1 and enhanced absorption on C-2), plus a further emission signal which is assigned to a partially acylated dimer product. The fact that in the reaction performed in this way, effect is observed on C-2 of compound **4b**, confirms the postulated influence of ketyl on the relaxation of sterically accessible nuclei. Here the influence of ketyl on the nuclei of the diamagnetic anion is markedly weakened by the equilibrium reaction (eqn 2e).

The weak emission signal on C-5 of compound **3a** probably originates in a combination of the acetyl radical with ketyl. In the given case, the acetyl radical can be generated by electron transfer to acetic anhydride. The combination of acetyl radical with ketyl can participate on the overall reaction only in a very minor way due to the instability of the acetyl radical. Polarization of C-5 is very weak also in reactions of dianions where the transfer from dianion to acetic anhydride has been proved.⁷

The CIDNP effects in ¹H NMR spectra in reactions of stable ion-radicals have so far only been observed with mixing of radicals in low magnetic field¹¹ (with the exception of effects in ¹⁹F NMR spectra in reactions of naphthalene sodium with parafluorobenzylhalogenides²³). For comparison we have followed by this technique also the presently studied reactions.

Flow measurement of ¹³C CIDNP effects during the mixing of reaction components in low field poses some experimental problems (good mixing of reactants, completion of the reaction in the space of low magnetic field, ¹H decoupling). The interpretation of the results is also more complicated. At this point we can only state that the ¹³C CIDNP effects at low field are of comparable intensity as for mixtures reacting at high field, but the spectra are qualitatively different. A strong dependence of the effects (phase of polarization) on small changes of magnetic field intensity (in the range 0-60 G) has also been observed. A study of ¹³C CIDNP effects at low field will be the subject of a subsequent communication.

CONCLUSION

In reactions of ketyls with acetic anhydride, the primary steps are nucleophilic reaction and heterolytic deprotonation. Application of strongly coordinating agents or greater dilution promote the latter reaction. In this way unstable radicals are formed yielding, by electron-transfer reaction with ketyl, benzophenone and an anion which generates the final products by a subsequent reaction proceeding by polar mechanism.

The reactions leading to CIDNP effects are spin-selective electron transfers between ketyl and acylated or protonated ketyl.

In reactions of benzophenone ketyls, 50% of benzophenone is always formed, while the changes of reaction conditions always only affect the ratio of compounds **2a** and **3a** which correlates with the CIDNP effect. Therefore we assume that the mechanism proposed for CIDNP is the predominant reaction mechanism.

The CIDNP effects depend on the relative rates of processes in the system, i.e. primary acylation or protonation, electron transfer and secondary reaction of the anion formed with acetic anhydride or benzophenone. These reactions determine the concentration of unreacted ketyl in the reacting mixture. The presence of ketyl as a stable radical considerably affects CIDNP, and can even lead to its complete disappearance. On benzophenone and fluorenone, CIDNP effects are not observed in presence of ketyl due to rapid electron transfer between molecules of ketyl and ketone. The presence of ketyl also increases the rate of relaxation of carbon nuclei on the phenyl and carbonyl groups of the anion, while the sterically hindered quaternary carbon (C-1) preserves at least partly its polarization up to the formation of the final product.

REFERENCES

- ¹G. O. Schlenck and G. Matthias, *Tetrahedron Letters* 699 (1967).
- ²G. Screttas and D. G. Georgiou, *Ibid.* 417 (1975).
- ³J. F. Garst and C. D. Smith, *J. Am. Chem. Soc.* **98**, 1520 (1976).
- ⁴I. M. Panayotov, I. B. Rashkov and I. N. Yukhnovski, *Europ. Polym. J.* **7**, 749 (1971).
- ⁵I. M. Panayotov and I. B. Rashkov, *Makromol. Chem.* **154**, 129 (1972).
- ⁶G. Mengoli and C. Vidotto, *Trans. Faraday Soc.* **66**, 2570 (1970).
- ⁷J. Honzl and M. Metalová, *J. Organometal. Chem.* **185**, 297 (1980).
- ⁸T. J. Curphey, L. D. Trivedi and T. Layloff, *J. Org. Chem.* **39**, 3831 (1974).
- ⁹G. Belot, C. Degrand and P. L. Compagnon, *Ibid.* **47**, 325 (1982).
- ¹⁰C. Degrand, P. L. Compagnon, G. Belot and D. Jacquin, *Ibid.* **45**, 1189 (1980).
- ¹¹J. F. Garst, In *Chemically Induced Magnetic Polarization* (Edited by A. R. Lepley and G. R. Closs), p. 223. Wiley, New York (1973).
- ¹²J. Lövy, J. Honzl and J. Jakes, *J. Magnetic Resonance*, in press.
- ¹³J. Stanton Pierce, W. W. Haden and R. D. Gano, *J. Am. Chem. Soc.* **67**, 408 (1945).
- ¹⁴A. L. Wilds and L. W. Beck, *Ibid.* **66**, 1688 (1944).
- ¹⁵J. F. Garst and J. A. Pacifici, *Ibid.* **97**, 1802 (1975).
- ¹⁶N. Hirota and S. I. Weissmann, *Ibid.* **86**, 2538 (1964).
- ¹⁷K. Nakamura, *Ibid.* **102**, 7846 (1980).
- ¹⁸H. M. Maurer, G. P. Gardini and J. Bargon, *J. Chem. Soc., Chem. Commun.* 272 (1979).
- ¹⁹R. Kaptein, *Ibid.* 732 (1971).
- ²⁰M. Broze and Z. Luz, *J. Chem. Phys.* **51**, 749 (1969).
- ²¹L. J. Aarson and F. C. Adam, *Can. J. Chem.* **50**, 1390 (1972).
- ²²R. Wilson, *J. Chem. Soc. (B)* 84 (1968).
- ²³J. W. Rakshys, *Tetrahedron Letters* 4745 (1971).
- ²⁴T. Takeshita and N. Hirota, *J. Am. Chem. Soc.* **93**, 6421 (1971).